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Bisoxamine  $\text{CH}_2(-\text{O}-\text{NH}_2)_2$  Salts"

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(Statement A)

The Synthesis and Characterization of Methylene Bisoxamine  
CH<sub>2</sub>(-O-NH<sub>2</sub>)<sub>2</sub> Salts

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ABSTRACT

A large family of energetic salts were made using methylene bisoxamine, CH<sub>2</sub>(-O-NH<sub>2</sub>)<sub>2</sub>, a dibasic, geminal oxyamine of methane. Single salts including the nitrate, perchlorate, dinitramide, and nitroformate, and doubly protonated methylene bisoxamine salts, nitrate, perchlorate and bisdinitramide, were all synthesized in good to high yields, from simple acid-base reactions with the corresponding acid forms of energetic anions. All of the salts were characterized by

vibrational (IR, Raman), multinuclear nmr ( $^1\text{H}$ ,  $^{13}\text{C}$ ), and DSC studies. The single crystal X-ray diffraction study was carried out on the double perchlorate salt. Initial safety studies (impact and friction), were carried out on most of the new materials, as well as the thermal stability of these salts at 75°C.

### INTRODUCTION

Ammonium perchlorate has been the oxidizer in many solid propellants for decades, due to its high density and high oxygen content.<sup>1</sup> The recent discovery of dinitramide salts, most notably ammonium dinitramide (ADN)<sup>2-5</sup>, along with the large release of decades-old Russian efforts<sup>6-12</sup>, has led a resurgence in the field of propellant ingredients. Workers in the field have been investigating other energetic salt systems, including 3,3-dinitroazetidine<sup>13</sup>, 3, 6-dihydrazino-1, 2, 4, 5-tetrazine<sup>14</sup>, bitetrazolates<sup>15</sup>, polyammonium salts<sup>16</sup>, nitrodicyanomethanide salts<sup>17</sup>, dinitrotriazole salts<sup>18, 19</sup>, and the recently reported oxyamine salts<sup>20</sup>. Others have incorporated the use of hydroxylammonium salts<sup>21-26</sup> as oxidizers in propellant systems. Despite the high performance of hydroxylammonium salts, many have been plagued by compatibility, stability, and sensitivity issues.

In our laboratories, we are investigating energetic salts, which have several inherent advantages, including high densities, negligible vapor pressure, and ease of handling. We have investigated energetic salts based on methylene bisoxamine,  $\text{CH}_2(\text{ONH}_2)_2$ . This geminal oxyamine of methane is not new, it was first synthesized in the late 1960's at Edwards AFB, including scale up efforts with the double perchlorate

salt.<sup>27-29</sup> Unfortunately, the material was dropped as a solid propellant ingredient, due to sensitivity and compatibility issues. Herein, we report our reinvestigation of methylene bisoxamine energetic salts, including the synthesis, characterization, a single crystal x-ray diffraction study of the double perchlorate salt, and initial safety studies.

#### EXPERIMENTAL

Methylene bisoxamine was prepared according to previously published methods.<sup>27-29</sup> The water-like liquid was distilled, and once its purity defined by  $^1\text{H}$  and  $^{13}\text{C}$  nmr, it was stored under nitrogen in a Schlenk flask. **WARNING!** Several of these materials were found to be friction and impact sensitive, most notably, the dinitramide salts. Extensive safety precautions including safety shields, tongs, leather gloves, heavy aprons, and face shields were used in the synthesis, handling and testing of all of these materials. Similarly, unexplainable explosions were encountered with the dinitrate and bis(dinitramide) salts. Nitric acid,  $\text{HNO}_3$  (69-70% by weight;  $\text{H}_2\text{O}$  solution; A.C.S. reagent grade) was purchased from Aldrich Chemical Company, and used without further purification. Perchloric acid,  $\text{HClO}_4$  (70.0% by weight,  $\text{H}_2\text{O}$  solution; Baker Reagent grade) was used as received. Ammonium dinitramide,  $\text{NH}_4\text{N}(\text{NO}_2)_2$ , was synthesized at SRI, Int., and after Raman spectroscopy revealed low  $\text{NO}_3^-$  content, and was stored in a brown bottle inside a nitrogen filled glove box. Trinitromethane ( $\text{H-C}(\text{NO}_2)_3$ ) was graciously donated from Dr. Karl Christe (ERC, Inc.) as a 37% by weight aqueous solution. The trinitromethane was extracted into 1,2 dichloroethane, with the

resulting dilute solution dried with fresh magnesium sulfate.<sup>30</sup> It was transferred under nitrogen purge to a large glass vessel sealed by a Teflon stopcock. The weight concentration of  $\text{H-C(NO}_2)_3$  was determined by multiple titrations with a standardized aqueous solution of potassium hydroxide. Methanol,  $\text{CH}_3\text{OH}$ ; Ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ ; and 2-Propanol,  $(\text{CH}_3)_2\text{CH-OH}$ , (ACS reagent grade; both distilled from sodium metal), and acetonitrile,  $\text{CH}_3\text{CN}$  and  $\text{CH}_2\text{Cl}_2$  (HPLC grade; both distilled from calcium hydride); diethyl ether (distilled from sodium metal / benzophenone); ethyl acetate (ACS reagent grade, low water, was used as received). All solvents were purchased from Aldrich Chemical Company and all were degassed using a liquid nitrogen freeze-thaw vacuum procedure. All solvents and reaction products were stored inside glass vessels, which were sealed with Teflon screw-cap plugs, and were equipped with #15 O-ring fittings.

Infrared spectra were recorded as KBr disks (using a KBr disk as a reference background) on a Nicolet 55XC FT-IR spectrometer from 4000-400  $\text{cm}^{-1}$ . Raman spectra were recorded in pyrex melting point capillaries on Bruker Model FRA 106/S Equinox 55 Raman spectrometer equipped with a 1.06 micron IR excitation laser. NMR experiments were carried out by dissolving the salts in dry  $\text{CD}_3\text{OD}$  or  $\text{CD}_3\text{S(=O)CD}_3$  in 5mm nmr tubes, and the  $^1\text{H}$  and  $^{13}\text{C}$  spectra recorded on a Bruker Spectrospin DRX 400 MHz Ultrashield<sup>TM</sup> NMR. Thermal analyses were carried out in hermetically sealed, coated aluminum pans on a Thermal Analyst 200, Dupont Instruments 910 Differential Scanning Calorimeter. Samples were prepared and sealed inside a nitrogen-filled glove box, and once the pans were inside the DSC cell, the cell was flushed with 10 mL per minute of nitrogen gas purge, during heating cycles (10 C/min). Elemental

analyses of most of the samples were carried out by Galbraith Laboratories, Inc., of Knoxville, TN.

Methylene bisoxyamine mononitrate,  $[\text{CH}_2(\text{ONH}_2)(\text{ONH}_3)^+]_1[\text{NO}_3^-]_1$ : Under nitrogen conditions a Schlenk flask was charged with 0.5001 g, 6.40 mmol, of methylene bisoxyamine. The flask was attached to a double manifold, evacuated, and then charged with dry nitrogen. Methylene chloride, 14 mL, was added through a disposable syringe along with a Teflon stir bar under nitrogen flow. Concentrated nitric acid, 0.6051 g, 9.60 mmol, was added with a disposable glass pipet under nitrogen flow. The reaction mixture, which was a clear, homogeneous solution with a white precipitate, was stirred for one hour at ambient temperature. At the end of one hour the stir bar was removed, and the liquid was decanted away from the white precipitate under nitrogen flow into a second Schlenk flask. The precipitate was washed with three aliquots, 10ml of diethyl ether under nitrogen flow. The precipitate was dried using a high vacuum over night. The next day, the white crystalline product, methylene bisoxyamine mononitrate, remained in very high yield, 0.8955 g, 6.34 mmol, or 99.1% of theory. Excellent crystals were formed from layering a concentrated methanol solution with diethyl ether, with subsequent storage at 4° C. M.P. 112°C by DSC.

IR ( $\text{cm}^{-1}$ ): 3308, 3248, 3099, 3018, 2779, 2721, 2591, 2426, 2400, 2394, 2054, 1762, 1579, 1462, 1419, 1398, 1383, 1354, 1283, 1241, 1143, 1049, 981, 870, 833, 819, 717, 706, 625, 543, 494.

Raman ( $\text{cm}^{-1}$ ): 3247, 3151, 3018, 2968, 2894, 2776, 1459, 1399, 1048, 986, 869, 855, 716, 706, 359, 302, 286, 99, 83, 66.

$^1\text{H}$  NMR: ( $\text{d}_6$ -dmsO) +8.694 ppm (rel. peak area 4.971), +5.001 (rel. peak area 2.000).

$^{13}\text{C}$  NMR: ( $\text{CD}_3\text{OD}$ ) +102.017 ppm singlet.

Elemental analysis: Theory. %C 8.51; %H, 5.00; %N, 29.78. Found. %C 8.71; %H, 5.06, %N, 28.80.

Methylene bisoxamine dinitrate,  $[\text{CH}_2(\text{ONH}_3)_2]^+[(\text{NO}_3)_2]^-$ : Under nitrogen conditions, a Schlenk flask was charged with 0.5156 g, 6.60 mmol, of methylene bisoxamine. The flask was attached to a double manifold, evacuated, and then charged with dry nitrogen. Methanol, 15 mL, was added through a disposable syringe along with a Teflon stir bar under nitrogen flow. Concentrated nitric acid, 1.2681 g, 20.1 mmol, was added with a disposable glass pipet, while stirring in an ice bath, under nitrogen flow. The reaction mixture, which was a clear, homogeneous solution, was stirred for one hour. At the end of one hour the stir bar was removed, and the liquid was decanted away from the white precipitate, which had formed, into a second Schlenk flask. The precipitate was washed with three aliquots, 10mL, diethyl ether under nitrogen flow. The precipitate was dried using a high vacuum for 1.5 hours. The white crystalline product, methylene bisoxamine dinitrate, remained in good yield, 1.0630 g, 5.20 mmol, or 78.8% of theory. M.P. 130°C by DSC.

IR ( $\text{cm}^{-1}$ ): 3167, 3153, 2896, 2830, 2787, 2717, 2674, 2648, 2594, 1932, 1766, 1751, 1600, 1554, 1496, 1486, 1448, 1384, 1355, 1315, 1211, 1167, 1111, 1044, 1036, 996, 888, 875, 832, 825, 720, 602, 529, 515, 500, 410, 403.

Raman ( $\text{cm}^{-1}$ ): 3144, 3045, 2988, 2775, 1566, 1447, 1405, 1332, 1170, 1045, 993, 888, 874, 723, 709, 526, 358, 153, 125, 83.

$^1\text{H}$  NMR: ( $d_6$ -dmso) +10.091 ppm (rel. peak area 6.305), +5.351 ppm (rel. peak area 2.000).

$^{13}\text{C}$  NMR: ( $d_6$ -dmso) +98.561 ppm singlet.



Elemental analysis: Theory. %C 5.88; %H, 3.95; %N, 27.45. Found. %C 6.10; %H, 3.97; %N 26.25.

Methylene bisoxyamine monoperchlorate,  $[\text{CH}_2(\text{ONH}_2)(\text{ONH}_3)^+][\text{ClO}_4^-]$ : A

Schlenk flask was charged with 0.4985 g, 6.38 mmol, of methylene bisoxyamine. The flask was attached to a double manifold, evacuated, and then charged with dry nitrogen. Acetonitrile, 15 mL, was added along with a Teflon stir bar under nitrogen flow. Concentrated perchloric acid 0.9435g , 6.57 mmoles, was added with a disposable glass pipet under nitrogen flow. The clear, homogeneous reaction solution was stirred for one hour at ambient temperature. At the end of one hour, the stir bar was removed, and the solution was layered with 25 ml of diethyl ether. The next day, the precipitate was washed with 3 aliquots, 5 ml each, of diethyl ether and dried under high vacuum. The white crystalline product, methylene bisoxyamine monoperchlorate, remained in reasonable yield, 0.7972 g, 4.46 mmol, or 69.9% of theory. M.P. 131°C by DSC.

IR ( $\text{cm}^{-1}$ ): 3323, 3283, 3274, 3212, 2972, 2893, 2698, 2360, 1594, 1572, 1542, 1497, 1455, 1444, 1380, 1277, 1249, 1222, 1084, 1039, 982, 940, 931, 863, 625, 588, 529, 508.

Raman ( $\text{cm}^{-1}$ ): 3267, 3028, 2970, 1459, 1378, 1295, 1131, 1081, 1056, 987, 934, 914, 871, 847, 628, 467, 458, 211, 150, 84.

$^1\text{H}$  NMR: ( $\text{d}_6$ -dmsO) +8.497 ppm (rel. peak area 5.080), +5.019 ppm (rel. peak area 2.000).

$^{13}\text{C}$  NMR: ( $\text{d}_6$ -dmsO) +100.380 ppm singlet.

Elemental analysis: Theory. %C 6.72; %H, 3.95; %N, 15.69. Found. %C 6.88; %H, 3.89; %N, 15.58.

Methylene bisoxamine diperchlorate,  $[\text{CH}_2(\text{ONH}_2)(\text{ONH}_3)_2]^+[(\text{ClO}_4)_2]^-$ :

A Schlenk flask was charged with 0.4010 g, 5.13 mmol, of methylene bisoxamine. The flask was attached to a double manifold, evacuated, and then charged with dry nitrogen. Ethanol, 15ml, was added along with a Teflon stir bar under nitrogen flow. Concentrated perchloric acid, 70% reagent grade, 1.8956 g, 18.8 mmol, was added with a disposable glass pipet under nitrogen flow. The reaction mixture, which was a clear, homogeneous solution, was stirred for one hour at ambient temperature. At the end of one hour, the stir bar was removed, and the solution was layered with 25 ml of diethyl ether. The next day, the solution was completely evacuated and the precipitate was re-dissolved in a minimal amount of ethanol, 5 ml, and layered with 30 ml diethyl ether.

Subsequent layering with diethyl ether was required to force the crystals out (50 ml). The precipitate was washed with 3 aliquots of 5 ml diethyl ether and dried under high vacuum. The clear crystalline product, methylene bisoxamine diperchlorate, remained in modest yield, 1.0564g, 3.78 mmol, or 45.9% of theory. M.P. 127°C by DSC.

IR ( $\text{cm}^{-1}$ ): 3202, 2904, 2785, 2718, 2694, 2674, 2649, 2595, 1944, 1576, 1555, 1524, 1495, 1487, 1451, 1384, 1375, 1264, 1124, 1072, 1036, 997, 939, 879, 635, 625, 499.

Raman ( $\text{cm}^{-1}$ ): 3044, 2986, 2885, 2750, 1523, 1450, 1382, 1320, 1125, 1081, 1040, 1007, 941, 881, 625, 458, 351, 84.

$^1\text{H}$  NMR: ( $d_6$ -dmsO) +9.994 ppm (rel. peak area 6.111), +5.345 ppm (rel. peak area 2.000).

$^{13}\text{C}$  NMR: ( $d_6$ -dmsO) +98.790 ppm .

Elemental analysis: Theory. %C 4.30; %H, 2.89; %N, 10.04. Found %C 4.61; %H 2.74; %N 10.14

Methylene bisoxamine mononitroformate,  $[\text{CH}_2(\text{ONH}_2)(\text{ONH}_3)^+][\text{C}(\text{NO}_2)_3^-]$ :

Under nitrogen conditions a Schlenk flask was charged with 0.5533 g, 7.08 mmol, of methylene bisoxamine. The flask was attached to a double manifold, evacuated, and then charged with dry nitrogen. Methylene chloride, 10 ml, was added along with a Teflon stir bar under nitrogen flow. Trinitromethane, or nitroform, 1.0704 g, 7.08 mmol, was added with a disposable glass pipet under nitrogen flow. The bright yellow reaction mixture was stirred for one hour. At the end of one hour, the stir bar was removed, and the liquid was decanted away from the bright yellow precipitate. The precipitate was washed with three 10 ml aliquots of diethyl ether. The precipitate was dried using a high vacuum over night. The bright yellow crystalline product, methylene bisoxamine mononitroformate, remained in good yield, 1.4755 g, 6.44 mmol, or 90.8% of theory. M.P. 107°C by DSC.

IR ( $\text{cm}^{-1}$ ): 3304, 3284, 3240, 3212, 3115, 3002, 2951, 2874, 2700, 2348, 1593, 1568, 1532, 1513, 1485, 1444, 1418, 1384, 1371, 1274, 1246, 1175, 1149, 1130, 1038, 983, 865, 794, 737, 733, 722, 657, 637, 500, 484, 462.

Raman ( $\text{cm}^{-1}$ ): 3758, 3612, 3305, 3240, 3140, 3016, 2963, 2888, 2740, 2467, 2379, 2308, 1414, 1376, 1289, 1248, 1236, 1160, 1149, 869, 855, 789, 786, 725, 463, 436, 261, 249, 150, 109, 84, 71.

$^1\text{H}$  NMR: ( $d_6$ -dmsO) +8.371 ppm (rel. peak area 5.000), +5.019 ppm (rel. peak area 1.926).

$^{13}\text{C}$  NMR: ( $d_6$ -dmsO) +150.288 ppm singlet ( $\text{C}(\text{NO}_2)_3^-$ ), +100.470 ppm singlet.

Elemental analysis: Theory. %C 10.48; %H, 3.07; %N, 30.56. Found. %C 10.76; %H, 3.08; %N, 29.20.

Methylene bisoxyamine monodinitramide,  $[\text{CH}_2(\text{ONH}_2)(\text{ONH}_3)^+][\text{N}(\text{NO}_2)_2^-]$ :

The following reaction was carried out in total darkness, with only the assistance of a red light. Methanol, reagent grade, 18 ml, was added to 1.7045 g, 13.7 mmol, of ammonium dinitramide, which resulted in the complete dissolution of the salt. A 1000 ml round bottom flask was charged with 1.0727 g, 13.7 mmol, of methylene bisoxyamine. Methanol, 100 ml, was added along with a Teflon stir bar and placed under the chromatography column. The chromatography column had previously been charged with a large amount of DOWEX<sup>®</sup> strong cation exchange resin. The ammonium dinitramide solution was transferred to the top of the column. The flask was rinsed with three aliquots, 30 ml each, of methanol. The solution was then eluted through the column, with three aliquots, 50 ml each, of methanol, which was subsequently added when the solvent level was just above the ion exchange bed. At the end of the elution, the reaction flask was removed, and the solvent removed by roto-evaporator. The product, a viscous oil, was transferred to a pre-weighed Schlenk flask, under nitrogen flow, with a minimal amount of methanol, 20 ml. The solvent was evacuated off with a high vacuum. The white crystalline product, methylene bisoxyamine monodinitramide, remained in modest yield, 1.5556 g, 8.40 mmol, or 57.4%. Crystals were formed from layering a concentrated methanol solution with diethyl ether, with subsequent storage at 4° C. M.P. 96°C by DSC.

IR ( $\text{cm}^{-1}$ ): 3748, 3328, 3284, 3253, 3090, 2742, 2347, 2041, 1983, 1752, 1541, 1460, 1437, 1384, 1344, 1334, 1299, 1175, 1133, 1026, 996, 873, 853, 827, 758, 731, 657, 637, 469, 407.

Raman ( $\text{cm}^{-1}$ ): 3252, 2960, 1456, 1334, 1170, 1048, 967, 881, 852, 825, 797, 750, 491, 322, 294, 232, 147, 103, 83, 34.

$^1\text{H}$  NMR: ( $d_6$ -dmso) +8.458 ppm (rel. peak area 5.001), +5.012 ppm (rel. peak area 2.000)

$^{13}\text{C}$  NMR: ( $d_6$ -dmso) +100.339 ppm singlet.

Elemental analysis: Theory. %C 6.48; %H, 3.81; %N, 37.83. Found. Not determined sample detonated at Galbraith Laboratories 9 consecutive times.

Methylene bisoxyamine bis(dinitramide)  $[\text{CH}_2(\text{ONH}_3^+)_2][(\text{N}(\text{NO}_2)_2^-)_2]$ :

The reaction was carried out in similar fashion to the monodinitramide salt. Methanol, 37 ml, was added to 3.6381 g, 29.3 mmol, of ammonium dinitramide, which resulted in the complete dissolution of the salt. A 1000 ml round bottom flask was charged with 1.1483 g, 14.7 mmol, of methylene bisoxyamine. Methanol, 100 ml, was added along with a Teflon stir bar and placed under the chromatography column. The ammonium dinitramide solution was transferred to the top of the column. The flask was rinsed with three aliquots, 30 ml each, of methanol. The solution was then eluted through the column, with three aliquots, 50 ml each, of methanol, which was subsequently added when the solvent level was just above the ion exchange bed. At the end of the elution, the reaction flask was removed, and the solvent removed by roto-evaporator. The product, a viscous oil, was transferred to a pre-weighed Schlenk flask, with a minimal amount of methanol, 15 ml. The solvent was evacuated off with a high vacuum. The viscous, oily product, methylene bisoxyamine bisdinitramide, remained in good yield, 3.5365 g, 12.1 mmol, or 74.9%. Crystals were formed by layering an ethyl acetate solution with ether, with subsequent storage at 4°C. M.P. broad, 85-95°C by DSC.

IR ( $\text{cm}^{-1}$ ): 3230, 3061, 2906, 2873, 2790, 2730, 2674, 2634, 2594, 1944, 1545, 1493, 1480, 1434, 1381, 1270, 1232, 1217, 1190, 1122, 1029, 1017, 996, 880, 831, 762, 750, 731, 499.

Raman ( $\text{cm}^{-1}$ ): 3270, 3111, 3045, 2980, 2870, 2736, 1659, 1562, 1505, 1445, 1326, 1244, 1326, 1244, 1170, 1090, 1037, 969, 888, 827, 755, 678, 488, 306, 103, 35.

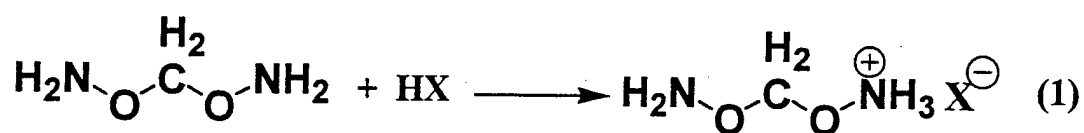
$^1\text{H}$  NMR: ( $d_6$ -dmsO) +10.281 ppm (rel. peak area 6.289), +5.371 ppm (rel. peak area 2.000).

$^{13}\text{C}$  NMR: ( $d_6$ -dmsO) +98.434 ppm singlet.

Elemental analysis: Theory. %C 4.11; %H, 2.76; %N, 38.35. Not carried out as sample exploded in drybox.

#### SYNTHESIS AND CHARACTERIZATION OF THE 1:1 SALTS OF METHYLENE BISOXYAMINE

The methylene bisoxyamine molecule has two oxyamine, ( $-\text{O}-\text{NH}_2$ ), functional groups, with both terminal amine groups being basic. The simple acid base reaction of methylene bisoxyamine with one equivalent of a strong acid gives the corresponding protonated species,  $[\text{CH}_2(-\text{ONH}_2)(-\text{ONH}_3)]^+$ , which then pairs with the conjugate base of the starting acid, to form stable, crystalline salts. (Reaction 1)



Where  $\text{HX} = \text{HNO}_3, \text{HClO}_4,$   
 $"\text{HN}(\text{NO}_2)_2", \text{HC}(\text{NO}_2)_3$

Several spectral techniques were used to substantiate the proposed structures of the products. (See Table 1) Vibrational spectra yielded strong evidence that the methylene bisoxyamine molecule is protonated on the nitrogen atom of one of the  $\text{O}-\text{NH}_2$  groups, to form an  $\text{O}-\text{NH}_3^+$  group.

In both the infrared and Raman spectra of all the 1:1 salts with various anions, several bands have been affected. The most notable are the  $\text{-NH}_2$  stretches, which in the starting material, are three broad peaks located at 3310, 3224, and  $3155\text{ cm}^{-1}$ , in the infrared and 3318, 3243, and  $3161\text{ cm}^{-1}$  in the Raman. Upon formation of the salts, there is a shift of the  $\text{-NH}_2$  stretching frequencies of the unprotonated  $\text{-O-NH}_2$  group to slightly higher frequencies, 10-20  $\text{cm}^{-1}$  higher, with the appearance of  $\text{-NH}_3^+$  bands centered around  $3150\text{ cm}^{-1}$ . This is also accompanied with the appearance of a broad band in the infrared spectra, ranging from 2400 to  $2800\text{ cm}^{-1}$ , which is indicative of hydrogen bonding in  $\text{-NH}_3^+$  salts, and has been observed in many other amine systems upon nitrogen protonation.<sup>31-38</sup> A shift to higher frequencies for the C-H stretches, an average of  $30\text{ cm}^{-1}$ , was visible in the Raman spectra, with most of the 1:1 salts of methylene bisoxamine. (These shifts are not easily distinguished in the infrared spectra due to the broad  $\text{-NH}_3^+$  bands, which make assignments difficult in this region.) This effect has been noted in other amine systems upon protonation.<sup>39</sup> The other main prominent band, which is easily assigned in both vibrational spectra, is that of the  $\text{-O-NH}_2$  stretch. In the parent material, methylene bisoxamine, the  $\text{O-NH}_2$  stretch appears at  $840\text{ cm}^{-1}$  in the infrared, and as a strong Raman band at  $843\text{ cm}^{-1}$ . In all of the monoprotonated salts of methylene bisoxamine, this  $\text{O-NH}_2$  band has appears as two bands in both the infrared and Raman spectra. One band shifted up an average of  $30\text{ cm}^{-1}$ , and the other band appears at an average of  $15\text{ cm}^{-1}$  higher. This shift to higher frequency of the  $\text{-O-NH}_2$  stretch upon protonation, has been noted in the similar amine systems of methoxyamine<sup>40-43</sup> and hydroxylamine<sup>44-46</sup>. All of the expected

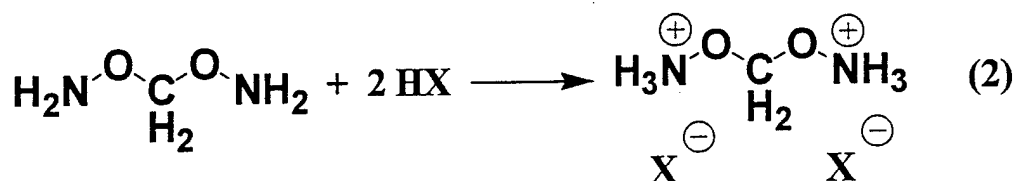
bands of the corresponding anions,  $\text{NO}_3^-$  <sup>47-51</sup>,  $\text{ClO}_4^-$  <sup>52</sup>,  $\text{N}(\text{NO}_2)_2^-$  <sup>53</sup>, and  $\text{C}(\text{NO}_2)_3^-$  <sup>54-56</sup>, were easily identifiable in both the infrared and Raman spectra, and matched the values of other, previously reported salts containing them.

NMR spectroscopy revealed both the purity, and significant nuclei shifts in both the proton and carbon atoms of the monoprotonated salts of methylene bisoxamine. (See Table 1) The starting material, methylene bisoxamine, has two signals in the  $^1\text{H}$  nmr spectrum, one, at +4.65 ppm downfield from  $(\text{CH}_3)_4\text{Si}$  (in  $\text{d}_6$ -DMSO), corresponding to the hydrogen atoms attached to the central carbon atom,  $\text{CH}_2(-\text{O}-\text{NH}_2)_2$ , and one broad peak, +6.05 ppm downfield, for the hydrogen atoms attached to the terminal  $-\text{NH}_2$  groups of the oxamine,  $\text{CH}_2(-\text{O}-\text{NH}_2)_2$ , with relative area of 2:4 upon integration. Upon protonation of one of the two  $-\text{O}-\text{NH}_2$  groups, both peaks are shifted downfield. The methylene protons are shifted an average of 0.4 ppm downfield from the starting methylene bisoxamine material, while the oxamine protons are shifted downfield an average of + 2.5 ppm. The integration of the two peaks relative to each other, works out to the expected 2:5 ratio of methylene protons to oxamine/oxammonium protons. These downfield shifts in  $^1\text{H}$  values, have been observed in other amine systems upon protonation, with strong acids.<sup>57</sup> In the  $^{13}\text{C}$  spectrum of methylene bisoxamine, a singlet at +102.21 ppm downfield from tetramethylsilane (in  $\text{d}_6$ -DMSO) was observed. Upon monoprotonation, the  $^{13}\text{C}$  signal of the methylene group shifted upfield an average of 1.5 ppm to a value of +100.5 ppm, which is indicative of protonation of the molecule, and is observed in many other amine systems upon protonation.<sup>58</sup>



# SYNTHESIS AND CHARACTERIZATION OF 1:2 SALTS OF METHYLENE BISOXYAMINE

Methylene bisoxamine is a diprotic base with two oxamine groups, and therefore can be protonated twice with strong acids to form the methylene bisoxammonium dication,  $[\text{CH}_2(-\text{O}-\text{NH}_3)_2]^{2+}$ . This was accomplished by reaction of methylene bisoxamine with two equivalents of concentrated perchloric and nitric acids, to form the double salts respectively. The double dinitramide salt was synthesized by using two equivalents of ammonium dinitramide passed through a strong cation exchange resin bed in methanol solution. (Reaction 2)



Where  $\text{HX} = \text{HNO}_3, \text{HClO}_4,$   
 $"\text{HN}(\text{NO}_2)_2"$

Decomposition incidents (deflagrations) of both the dinitrate and the bis(dinitramide) salts, have been experienced upon standing at room temperature. These incidents point to long-term stability problems of these salts, and extreme caution should be exercised when synthesizing and handling of any of the double salts of methylene bisoxamine. Attempts were made to synthesize the double nitroformate salt, however, only the mono salt was recovered. Apparently, nitroform is too weak of an acid to effect the double protonation of methylene bisoxamine.

Vibrational spectra, despite being dominated by the strong bands of the corresponding anions, offered strong evidence for the double protonation of the methylene bisoxamine molecule on the amine nitrogen atoms of two oxamine groups. (See Table 1) In both the infrared and

Raman spectra, there is a total absence of  $\text{-NH}_2$  stretches, with the subsequent large, broad bands indicative of  $\text{-NH}_3^+$  stretches, centered around  $3150\text{ cm}^{-1}$ . In the infrared spectra of all the double salts, there was a large broad band of absorbance ranging from approximately  $2400\text{ cm}^{-1}$  to  $2800\text{ cm}^{-1}$ , which has been identified by previous authors as a result of hydrogen bonding in various  $\text{-NH}_3^+$  salts.<sup>31-38</sup> The other major, easily observed shift in both the infrared and Raman spectra, was that of  $\text{-O-NH}_3^+$  stretch. In the parent material, methylene bisoxamine, the  $\text{O-NH}_2$  stretch appears at  $840\text{ cm}^{-1}$  (infrared), and at  $843\text{ cm}^{-1}$  (Raman). In the doubly protonated species, the methylenebisoxammonium cation,  $\text{CH}_2(\text{-O-NH}_3)^{2+}$ , this band has been significantly shifted to higher frequencies,  $40\text{-}50\text{ cm}^{-1}$  in both the infrared and Raman spectra. There is only one other example of a multiply protonated oxyamine material, 1, 2- ethylenebisoxamine dihydrobromide, unfortunately, no vibrational data was given<sup>59</sup>. Hence, there is nothing to compare with, but the shift of the  $\text{O-NH}_2$  stretch to even higher frequencies upon double protonation of methylene bisoxamine, is reasonable in light of the evidence from the shifts observed upon monoprotection of the neutral material. The vibrational spectra are dominated by the bands of the corresponding anions, and the observed frequencies are well in agreement with well-established examples of  $\text{NO}_3^-$ <sup>47-51</sup>,  $\text{ClO}_4^-$ <sup>52</sup>,  $\text{N}(\text{NO}_2)_2^-$ <sup>53</sup>, and require no further discussion.

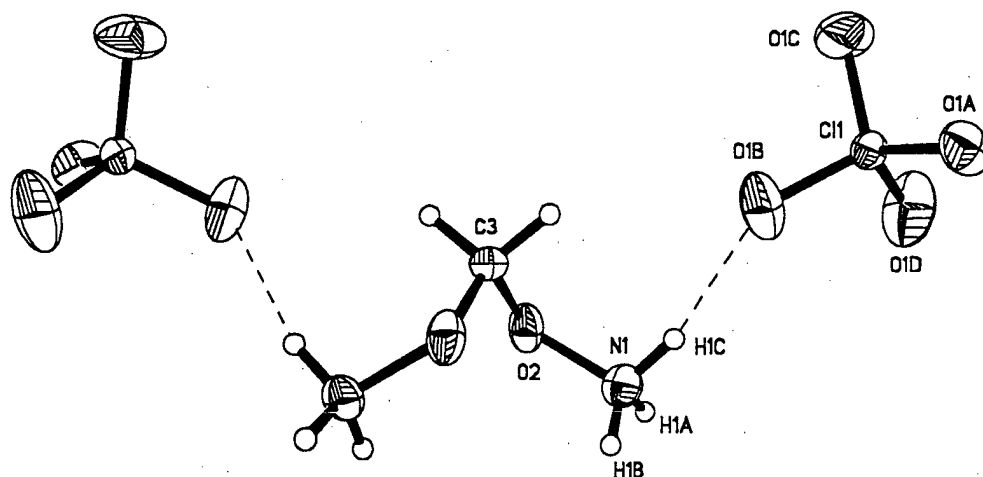


Figure 1. An ORTEP plot of the full salt unit. The asymmetric unit is just the labeled atoms above,  $\frac{1}{2}$  of the full salt. A crystallographic two-fold symmetry axis bisects the cation; it is a vertical axis in this view.<sup>60</sup>

$^1\text{H}$  and  $^{13}\text{C}$  nmr studies of the methylene bis(oxyammonium) salts revealed pure compounds with significant shifts in observed peaks in the corresponding spectra. (See Table 1) In the  $^1\text{H}$  spectra, the methylene proton signal,  $\text{CH}_2(-\text{O}-\text{NH}_2)_2$ , shifted downfield an average of 0.6 ppm, from the neutral starting material, to a value of +5.3 ppm downfield from TMS. The proton signal associated with  $-\text{O}-\text{NH}_3^+$  hydrogen atoms, was significantly shifted downfield from the starting material. An average shift value of +10.1 ppm downfield from TMS, is a rather large 4 ppm downfield shift from the starting material. Integration of peak areas of methylene protons versus that of oxyammonium protons, were close to the expected 2:6 ratio. In the  $^{13}\text{C}$  spectra, only one peak was observed in the spectra of all the doubly protonated species, and it was shifted upfield from the starting material, by an average value of 3.5 ppm, to

an average value of +98.6 ppm downfield from TMS. These findings agree well with other shift values reported for other doubly protonated amine salts.<sup>57, 58</sup>

#### SMALL SCALE SAFETY TESTING AND THERMAL STABILITY STUDIES

All of the new salts were tested for impact and friction sensitivity, as these are very important characteristics of any new energetic material. At AFRL, new materials are impact tested on an Olin-Mathieson style drop weight tester. A small amount of preweighed sample, usually around 20 milligrams, was placed in a steel cup for each test. A standard of HMX, 6 micron size, tested prior to the new energetic materials as a standard, gave a value of 34 kg-cm for five consecutive negative results. Drop heights were measured in centimeters with a falling mass, and a minimum drop height is considered for five consecutive drops at a specific height and mass, with no change in the sample. For friction testing, a Julius Peters sliding friction tester was used. This involves sliding a ceramic pin under a known load of force, across a sample placed on a small, rectangular ceramic plate. A positive in this test is usually identified by discoloration, spark, smoke, or detonation of the sample. As can be seen from Table 2, a wide array of values in sensitivity for the salts was obtained. Most of the salts were more impact sensitive than HMX. Impact sensitivities ranged from a moderate value of 110 kg-cm, to less than 5 kg-cm for the bisdinitramide salt. A five kg-cm impact indicates an excessively sensitive material. Results of friction testing revealed that the methylene bisoxayamine salts range from moderately sensitive, at 15.2 kg, to extremely sensitive, <0.45 kg, with both the monodinitramide and monoperoxchlorate salts being frightening; both exhibited values less than

0.45 kg. This demonstrated that they are extremely sensitive materials. On the basis of small-scale safety tests, most methylene bisoxamine salts should not ever be scaled-up.

One of the most difficult hurdles for a new propellant ingredient to pass, is the thermal stability test at elevated temperatures, in this case 75°C. In this test, a small amount (approximately 20 mg) of new material was placed in a small, pre-weighed quartz bucket, and carefully placed on a balance beam, inside a vertical, thermogravimetric analyzer (TGA). The sample cell containing the quartz bucket was flushed with ultrapure nitrogen gas for 1 hour, and then heated isothermally at 75°C for 2 days (48 hours). The drop in sample weight was monitored as a function of time. Some of the samples contained small amounts of residual solvent. This resulted in an initially high rate of weight loss in the sample. However, after a short time period, drop in sample weight became almost linear. Linear weight loss was assumed to be due to sample decomposition. Using simple regression analysis, the linear decomposition rate,  $n$ , was calculated. For most of the samples, the DSC was an initial indicator of how long-term stable a material was. Initial studies revealed that all materials tested had undesirable results with significant mass losses in short periods of time. These unfortunate results essentially eliminates them from any further propellant ingredient investigations.

#### SUMMARY AND CONCLUSIONS

A large array of energetic salts based on methylene bisoxamine,  $\text{CH}_2(\text{-ONH}_2)_2$ , a base capable of being either singly or doubly protonated, were synthesized in high yields and in high purity in facile routes. The 1:1 salts of nitrate, perchlorate, dinitramide, and

nitroformate, along with the 1:2 salts of dinitrate, bis(dinitramide), and diperchlorate, were characterized by multinuclear nmr ( $^1\text{H}$ ,  $^{13}\text{C}$ ), vibrational spectroscopy (infrared and Raman), mass balance, DSC studies, and satisfactory elemental analyses. A single crystal X-ray diffraction studies carried out on the double perchlorate salt revealed the expected molecular structure. Small-scale safety tests (impact and friction) carried out on this array, revealed that many were quite sensitive materials, and would not be safe to handle on a large scale. Initial thermal stability studies of the salts, carried at 75°C, revealed that all lost significant mass within a short amount of time. This result, along with the sensitivity issues, rule out any future propellant plans for methylene bisoxamine salts. It is not known whether the geminal oxamine functionality is unstable or oxamines as a whole are unstable. Further investigations into other bisoxamine systems are currently underway, in order to determine the viability of the O-NH<sub>2</sub> functional group in other energetic moieties.

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References Cited

- 1 Sutton, George P. "Rocket Propulsion Elements An Introduction to the Engineering of Rockets, 6<sup>th</sup> Edition" John Wiley & Sons, Inc. 1992, New York, NY.
- 2 Bottaro, J. C. ; Penwell, P. E. ; Schmitt, R. J. Synth. Commun. 1991, 21, 945.
- 3 Bottaro, J. C. ; Penwell, P. E. ; Schmitt, R. J. ; Ross, D. S. U. S. Patent # 5,198,204, March 30, 1993.
- 4 Bottaro, J. C. ; Penwell, P. E. ; Schmitt, R. J. ; Baumberger, D. C. U. S. Patent # 5,316,749, May 31, 1994.
- 5 Bottaro, J. C. ; Penwell, P. E. ; Schmitt, R. J. ; Baumberger, D. C. U. S. Patent # 5,415,852, May 16, 1995.
- 6 Luk'yanov, O. A. ; Gorelik, V. P. ; Tartakovskii, V. A. Russ. Chem. Bull. 1994, 43, 89.
- 7 Luk'yanov, O. A. ; Konnova, Yu. V. ; Klimova, T. A. ; Tartakovsky, V. A. Russ. Chem. Bull. 1994, 43, 1200.
- 8 Luk'yanov, O. A. ; Anikin, O. V. ; Gorelik, V. P. ; Tartakovsky, V. A. Russ. Chem. Bull. 1994, 43, 1457.
- 9 Shlyapochnikov, V. A. ; Cherskaya, N. O. ; Luk'yanov, O. A. ; Gorelik, V. P. ; Tartakovsky, V. A. Russ. Chem. Bull. 1994, 43, 1522.
- 10 Luk'yanov, O. A. ; Shlykova, N. I. ; Tartakovsky, V. A. Russ. Chem. Bull. 1994, 43, 1680.
- 11 Luk'yanov, O. A. ; Agevnin, A. R. ; Leichenko, A. A. ; Seregina, N. M. ; Tartakovsky, V. A. Russ. Chem. Bull. 1995, 44, 108.

- 12 Shlyapochnikov, V. A. ; Oleneva, G. I. ; Cherskaya, N. O. ;  
Luk'yanov, O. A. ; Gorelik, V. P. ; Anikin, O. V. ; Tartakovsky,  
V. A. J. Mol. Struct. 1995, 348, 103.
- 13 Hiskey, M. A. U. S. Patent # 5,395,945, March 29, 1993.
- 14 Chavez, D. E. ; Hiskey, M. A. J. Energ. Mater. 1999, 17, 357.
- 15 Hiskey, M. A. ; Goldman, N. ; Stine, J. R. J. Energ. Mater.  
1998, 16, 119.
- 16 McKenney, R. L. ; Struck, S. R. ; Hildreth, R. A. ; Fryling, J. A.  
J. Energ. Mater. 1987, 5, 1.
- 17 Arulsamy, N. ; Bohle, S. D. ; Deletski, B. G. Inorg. Chem. 1999,  
38, 2709.
- 18 Lee, K. Y. ; Ott, D. G. U. S. Patent # 4,236,014, November 25,  
1980.
- 19 Ayyanger, N. R. ; Kalkote, U. R. ; Lugade, A. G. ; Nikrad, P. V.  
; Sharma, V. K. Bull. Chem. Soc. Japan 1983, 56, 3159.
- 20 Bottaro, J. C. ; Schmitt, R. J. ; Petrie, M. A. ; Penwell, P. E.  
U. S. Patent 6,096,774, August 1, 2000.
- 21 Biddle, R. A. ; Sutton, E. S. U. S. Patent # 4,527,389, July 9,  
1985.
- 22 Rothgery, E. F. ; Migliaro, F. W. U. S. Patent # 5,405,971,  
April 11, 1995.
- 23 Highsmith, T. K. ; Blau, R. J. ; Lund, G. K. U. S. Patent #  
5,682,014, October 28, 1997.
- 24 Barnes, M. W. ; Harris, B. D. ; Johnson, D. L. U. S. Patent #  
5,684,269, November 4, 1997.
- 25 Bruenner, R. S. ; Oberth, A. E. ; Clark, G. M. ; Katzakian, A.  
U. S. Patent # 5,837,931, November 17, 1998.
- 26 Wagaman, K. L. U. S. Patent # 6,001,197, December 14, 1999.



- 27 McDowell, C. S. ; Barnes, M. W. U. S. Patent # 3709920, January 9, 1973.
- 28 McDowell, C. S. ; Merrill, C. I. U. S. Patent # 3714199, January 30, 1973.
- 29 McDowell, C. S. ; Merrill, C. I. U. S. Patent # 3714200, January 30, 1973.
- 30 Frankel, M. B. ; Ranieri, F. D. ; Thompson, W. W. ; Witucki, E. F. ; Woolery, D. O. U. S. Patent # 4147731, April 3, 1979.
- 31 Liever, E. ; Levering, D. R. ; Patterson, L. J. Anal. Chem. 1951, 23, 1594.
- 32 Edsall, J. T. ; Scheinberg, H. J. Chem. Phys. 1940, 8, 520.
- 33 Chenon, B. ; Sandorfy, C. Can. J. Chem. 1958, 36, 1181.
- 34 Edsall, J. T. J. Chem. Phys. 1937, 5, 225.
- 35 Pelius, J. L. ; Pearson, D. P. J. Phys. Chem. 1953, 75, 2436.
- 36 Garfinkel, D. ; Edsall, J. T. J. Amer. Chem. Soc. 1958, 80, 3807.
- 37 Bellanto, J. Spectrochim. Acta 1960, 16, 1344.
- 38 Durig, J. R. ; Bush, S. F. ; Mercer, E. E. J. Chem. Phys. 1966, 44, 4238.
- 39 Ghazanfar, S. A. S. ; Edsall, J. T. ; Myers, D. V. J. Amer. Chem. Soc. 1964, 86, 559.
- 40 Davies, M. ; Spiers, N. A. J. Chem. Soc. 1959, 3971.
- 41 Buerger, H. ; Burczyk, K. ; Smrekar, O. Monatsh. Chem. 1969, 100, 766.
- 42 Sarykhanov, M. A. ; Parpiev, N. A. Zh. Neorg. Khim. 1970, 15, 1475.
- 43 Giguere, P. A. ; Liu, I. D. Can. J. Chem. 1952, 30, 948.
- 44 Redlich, O. ; Friedman, I. I. J. Amer. Chem. Soc. 1945, 67, 893.

- 45 Nightingale, R. E. ; Wagner, E. L. J. Chem. Phys. 1954, 22, 203.
- 46 Frasco, D. L. ; Wagner, E. L. J. Chem. Phys. 1959, 30, 1124.
- 47 Williamson, K. ; Li, P. ; Devlin, J. P. J. Chem. Phys. 1968, 48, 3891.
- 48 Nakagawa, I. ; Walter, J. L. J. Chem. Phys. 1969, 51, 1389.
- 49 Rousseau, D. L. ; Miller, R. E. J. Chem. Phys. 1968, 48, 3409.
- 50 Smith, D. ; James, D. W. ; Devlin, J. P. J. Chem. Phys. 1971, 54, 4437.
- 51 Janz, G. J. ; Kozlowski, T. R. J. Chem. Phys. 1964, 40, 1699.
- 52 Taylor, R. C. ; Vidalo, G. L. J. Amer. Chem. Soc. 1956, 78, 5999.
- 53 Christe, K. O. ; Wilson, W. W. ; Petrie, M. A. ; Michels, H. H. ; Bottaro, J. C. ; Gilardi, R. Inorg. Chem. 1996, 35, 5068.
- 54 Kamlett, M. J. ; Oesterling, R. E. ; Adolph, H. G. J. Chem. Soc. 1965, 5838.
- 55 Shakhor, I. N. ; Tselinskii, I. V. ; Gal'kovskaya, A. G. ; Mel'nikov, V. V. Zhurn. Organ. Khimii. 1967, 3, 489.
- 56 Mel'nikov, V. V. ; Nel'son, I. V. ; Shakhor, I. N. ; Tselinskii, I. V. Zhurn. Organ. Khimii. 1968, 4, 349.
- 57 Pouchert, C. J. The Aldrich Library of NMR Spectra Edition II, Volume I. 1983, Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.
- 58 Simons, W. W. (Ed.) The Sadtler Guide to Carbon-13 NMR Spectra. 1983, Sadtler Research Laboratories, Philadelphia, PA.
- 59 Bauer, L. ; Suresh, S. K. J. Org. Chem. 1963, 28, 1604.
- 60 Empirical formula :  $C_1 H_8 Cl_2 N_2 O_{10}$  ; Formula weight = 278.99  
; Temperature = 293(2) K ; Wavelength = 1.54178 Å ; Crystal system = Orthorhombic ; Space group = Pbcn ; Unit cell dimensions : a =

8.1506(4) Å ;  $\alpha = 90^\circ$  ;  $b = 11.7354(6)$  Å ;  $\beta = 90^\circ$  ;  $c = 9.6676(5)$  Å  
 ;  $\gamma = 90^\circ$ . Volume = 924.71(8) Å<sup>3</sup> ;  $Z = 4$ . Density (calculated) =  
 2.004 Mg/m<sup>3</sup>. Absorption coefficient = 6.904 mm<sup>-1</sup>.  $F(000) = 568$  ;  
 Crystal size : 0.25 x 0.40 x 0.40 mm<sup>3</sup>. Theta range for data  
 collection: 6.61 to 66.82°. Index ranges:  $-9 \leq h \leq 9$ ,  $-13 \leq k \leq 13$ ,  $-11 \leq l \leq 11$ . Reflections collected = 3440; Independent reflections:  
 798 [ $R(\text{int}) = 0.0735$ ] ; 'Observed' independent reflections : 733  
 [ $I(\text{obs}) > 2 \cdot \sigma(I)$ ]. Completeness to theta = 66.82° (97.0% ).  
 Absorption correction: Empirical (SADABS, Bruker). Refinement  
 method: Full-matrix least-squares on  $F^2$ . Data / restraints /  
 parameters: 798 / 13 / 71. Goodness-of-fit on  $F^2$  : 1.097. Final R  
 indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0725$ ,  $wR_2 = 0.2054$ . R indices (all  
 data) :  $R_1 = 0.0755$ ,  $wR_2 = 0.2083$ . Extinction coefficient:  
 0.025(3). Largest diff. peak and hole: 0.590 and -0.498 e.Å<sup>-3</sup> .  
 Selected bond distances (angstroms): C(3)-O(2) = 1.395(6); N(1)-  
 O(2) = 1.407(6); Cl(1)-O(1D) = 1.391(5); Cl(1)-O(1C) = 1.407(4);  
 Cl(1)-O(1B) = 1.413(4); Cl(1)-O(1A) = 1.418(4).